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## SPECIFICATION

### TITLE OF THE INVENTION

A POROUS DOUBLE METALLIC OXIDE AND ITS FABRICATION METHOD

### CLAIMS

1. A porous double metallic oxide formed on a supporter and having pores of a size 0.1 to 30  $\mu\text{m}$ .
2. A method for fabricating a porous double metallic oxide comprising the steps of forming a gel film of a metal oxide on a supporter, and forming a porous metallic oxide on the supporter with a hydrothermal process.

### DETAILED EXPLANATION OF THE INVENTION

[0001]

#### FIELD OF THE INVENTION

The invention relates to a porous double metallic oxide which can be used as an adsorbate, a catalyst carrier, a dielectric material for a plate for electronic components, a high frequency ceramic capacitor, a strip line filter or the like, a dielectric material for a piezoelectric actuator, and the like.

[0002]

#### PRIOR ART

Previously, a porous ceramic is fabricated with a following process.

[0003]

First, an organic binder is added to inorganic powders and they are mixed sufficiently to blend them uniformly. Then, many small organic resin balls of grain size of 50 to 60  $\mu\text{m}$  are added, and they are distributed uniformly. Then the mixture is formed to have a predetermined shape, and it is heated at a temperature of about 300 to 400  $^{\circ}\text{C}$ . In the heating, the resin balls as well as the organic binder disappear to form many holes. Next, the material including the many holes is sintered at a temperature of about 1,000 to 1,300  $^{\circ}\text{C}$ . Thus, the inorganic powders are sintered, and a porous glass ceramic is obtained.

[0004]

#### PROBLEMS TO BE SOLVED BY THE INVENTION

However, according to this method, after the inorganic and organic binders are mixed, the organic resin balls having a very different specific density from the inorganic

powders are added. Therefore, uniform mixing is difficult, and it takes a long time to mix the resin balls with the binders.

[0005]

Further, because the method needs many organic resin balls, the fabrication cost is high.

[0006]

Further, because the method needs many organic resin balls, it has relatively large holes larger than 50  $\mu\text{m}$ . Therefore, a porous ceramic having smaller holes cannot be provided.

[0007]

An object of the invention is to provide a porous double metallic oxide which solves the above problem.

[0008]

#### MEANS FOR SOLVING THE PROBLEM

The invention relates to a porous double metallic oxide formed on a supporter and having pores of a size 0.0 to 30  $\mu\text{m}$ .

[0009]

Further the invention relates to a method for fabricating a porous double metallic oxide comprising the steps of forming a gel film of a metal oxide on a supporter, and forming a porous metallic oxide on the supporter with a hydrothermal process.

[0010]

The metallic oxide is any material which can form a gel film on a supporter. For example, at least one of Ti, Bi, Zr, Pb and the like is used. The gel film can be fabricated by dissolving at least one of metallic compounds of Ti, Bi, Zr, Pb and the like in a solvent of water or alcohol and by applying the solution to the supporter, and by drying it in a temperature range between room temperature and 200 °C. The metallic compound is for example a compound not soluble easily in a solvent of water or alcohol such as a hydroxide, a halide such as a chloride, a nitrate, a phosphate, an oxide or an acetate of Ti, Bi, Zr, Pb or the like. Further, a metallic organic compound such as alcoxide of titanium can be used. By changing the viscosity of the solvent and the composition and the concentration of the metallic compound to be dissolved in the solvent, a gel film of a desired composition and of a desired thickness can be formed. If the gel film is too thick, it is liable to be peeled off at drying at room temperature. It is desirable that the thickness of the gel film is 0.1 to 100  $\mu\text{m}$ , more preferably 30 to 50  $\mu\text{m}$ .

[0011]

Any supporter can be used as far as a gel film of a metallic oxide is formed thereon. For example, it is made of a glass, heat-resistant glass, polyimide, titanium oxide, titanium metal, stainless steel or the like. The supporter has any shape as far as a gel film is formed thereon. For example, it has a shape of a plate, a thin film, a wavy plate, a shaft, a tube, a cube, a grain or the like. It is also possible to form a gel film on a desired area of a supporter. By performing a hydrothermal reaction after forming a gel film, a porous double metallic oxide having pore sizes of 1 to 30  $\mu\text{m}$  can be prepared.

[0012]

#### EMBODIMENTS

A method according to the invention suitable for fabricating a porous double metallic oxide is explained below with an example of amorphous Pb-Zr-O formed on a supporter.

[0013]

A Pb-Zr-O gel film is formed on a supporter made of a titanium film according to a following process. First, an aqueous solution of Pb and Zr chlorides is applied to the supporter, and it is dried for about two hours at a temperature between room temperature and 200 °C to form a gel film made of Pb and Zr of about 30  $\mu\text{m}$  thickness. When the gel film is formed, the concentration of metallic compounds of Pb, Zr and the like is controlled in order to change the pore size of the porous double metallic oxide to be obtained by hydrothermal treatment later. By decreasing the concentration of the metal oxide components in the gel film, a porous double metallic oxide having a larger cell size can be obtained, while by increasing the concentration of the metal oxide components in the gel film, a porous double metallic oxide having a smaller cell size can be obtained.

[0014]

Next, a hydrothermal reaction is performed with a conventional autoclave 1 as shown in Fig. 1. In the hydrothermal reaction, a solution for hydrothermal reaction is supplied into an inner case 4, and the supporter with the Pb-Zr-O gel film is put therein. In Fig. 1, reference numeral 2 denotes an outer case, and a heater 3 is set outside the outer case 2. The hydrothermal temperature is controlled by a temperature controller.

[0015]

The hydrothermal reaction is performed in an aqueous solution of Pb and Zr compounds or in an alkaline solution of 1-5 N KOH or the like at a reaction temperature of 120 to 200 °C at a pressure of saturated water vapor of 0.5 to 50  $\text{kg}/\text{cm}^2$  for 0.2 to 20 hours. According to the hydrothermal reaction, a porous Pb-Zr-O double metallic oxide

of thickness of 1 to 100  $\mu\text{m}$  is formed on a surface of the supporter to have pores of radii of 0.1 to 30  $\mu\text{m}$ . Then, electrodes films are formed on the double metallic oxide with a conventional process, for example with a silver paste. Thus, a piezoelectric film or the like can be fabricated. By performing the hydrothermal reaction constantly, the porous double metallic oxide has a uniform pore size. By controlling the hydrothermal reaction temperature and the reaction time, the porous double metallic oxide has a desired thickness.

[0016]

Because the porous double metallic oxide fabricated in the invention has very fine and uniform pores, it can be used favorably as an adsorbate, a catalyst carrier or the like. Further, it can also be used as a material for a dielectric material or a piezoelectric element. The resultant porous double metallic oxide is usually amorphous, and the as-fabricated oxide can be used as the adsorbate, the catalyst carrier or the like. When a crystalline material is requested, it is fired at about 600  $^{\circ}\text{C}$ . The firing is desirable for a dielectric material or the like in order to improve electric characteristics.

[0017]

## EXAMPLES

### Example 1

A PbO gel film is formed by using a titanium plate as a supporter, as explained below. After dissolving 0.06 mol of lead naphthenate in 10 ml of ethanol, the titanium plate is immersed therein and is pulled up therefrom. After drying the titanium plate, a gel film of 30  $\mu\text{m}$  thickness is obtained. The titanium plate 5 on which the PbO gel film is formed is set in the inner case 4 of the autoclave shown in Fig. 1, and a 1.0N KOH aqueous solution 6 is added. Then, a hydrothermal reaction is performed at a reaction temperature of 150  $^{\circ}\text{C}$  at a pressure of saturated water vapor of 4.0  $\text{kg}/\text{cm}^2$  for one hour. Then, a PbO film of 10  $\mu\text{m}$  thickness is obtained on the titanium plate 5. Fig. 2 shows a SEM photograph on a surface of the obtained film. It is found that the PbO film is an amorphous film having very fine pores of average size of 0.5  $\mu\text{m}$ . Fig. 3 shows an X-ray analysis diagram for a PbO film after one-hour firing, wherein black circles represent peaks due to Ti and white circles represent peaks due to Pb. It is confirmed that the porous film shown in Fig. 3 is a PbO film.

[0018]

### Example 2.

A stainless steel 5 on which a TiO gel film is formed is set in the inner case of the autoclave shown in Fig. 1, and a 0.5N KOH aqueous solution 6 is added. Then, a

hydrothermal reaction is performed at a reaction temperature of 180 °C at a pressure of saturated water vapor of 8.0 kg/cm<sup>2</sup> for two hours. Then, a TiO film of 10 μm thickness is obtained on the stainless steel plate 5. Fig. 4 shows a SEM photograph on a surface of the obtained film. It is found that the TiO film has very fine pores of average size of 0.7 μm. Fig. 5 shows an X-ray analysis diagram for a TiO film after one-hour firing. It is confirmed that the porous film shown in Fig. 5 is a TiO film.

[0019]

Example 3.

A heat-resistant glass plate 5 on which a Pb-Zr-TiO gel film is formed is set in the inner case of the autoclave shown in Fig. 1, and a distilled water 6 is added. Then, a hydrothermal reaction is performed at a reaction temperature of 120 °C at a pressure of saturated water vapor of 1.5 kg/cm<sup>2</sup> for ten hours. Then, a Pb-Zr-TiO film of 10 μm thickness is obtained on the glass plate 5. Fig. 6 shows a SEM photograph on a surface of the obtained film. It is found that the TiO film is a film having very fine pores of average size of 0.5 to 1.0 μm. Fig. 7 shows an X-ray analysis diagram for a TiO film after one-hour firing at 600 °C. It is confirmed that the film shown in Fig. 7 is a Pb(Zr<sub>0.5</sub>Ti<sub>0.5</sub>)O film.

[0020]

#### ADVANTAGES OF THE INVENTION

According to the invention, a double metallic oxide having very fine pores can be provided. According to the invention, a metal oxide film having a uniform pore size can be fabricated directly on a supporter in conditions of a relatively low temperature by using a simple hydrothermal reaction.

#### BRIEF EXPLANATION OF THE DRAWING

Fig. 1 is a sectional view of an autoclave used in the invention.

Fig. 2 is a SEM photograph of a grain structure of a porous metallic oxide obtained in the invention.

Fig. 3 is an X-ray analysis diagram of a porous metallic oxide obtained in the invention.

Fig. 4 is a SEM photograph of a grain structure of a porous metallic oxide obtained in the invention.

Fig. 5 is an X-ray analysis diagram of a porous metallic oxide obtained in the invention.

Fig. 6 is a SEM photograph of a grain structure of a porous metallic oxide obtained in the invention.

Fig. 7 is an X-ray analysis diagram of a porous metallic oxide obtained in the invention.

[EXPLANATION OF SIGNS]

1: Autoclave. 2: Outer case. 3: Heater. 4. Inner case, 5: Supporter. 6: Reaction liquid.